



Non-adsorbing polymers and yield stress of cement paste: Effect of depletion forces

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ABSTRACT

In this work, we study the effect of non-adsorbing polymers with molar masses varying over several decades in both dilute and semi-dilute regimes on the yield stress of cement and calcite pastes. In both suspensions, we measure an increase of yield stress, the magnitude of which mainly depends on the polymer concentration regimes. From interparticle force calculations, we show that non-adsorbing polymers are at the origin of interparticle attractive depletion forces. In the absence of superplasticizers, Van der Waals attractive forces are the dominant flocculating mechanism in the system and depletion forces resulting from non-adsorbing polymers are negligible. The repulsive forces that result from superplasticizers' steric contribution increase the average interparticle distance and therefore decrease the magnitude of the attractive van der Waals forces. In this latter system, attractive depletion forces induced by non-adsorbing polymers become important and greatly contribute to the flocculation mechanism.

1. Introduction and background

Chemical admixtures are fundamental components of cementitious materials allowing for the tuning of the material fresh and/or hardened properties. Admixtures such as superplasticizers, or the so-called flocculants, control the yield stress of the suspension by adsorbing at the surface of the particles and modifying the range, the magnitude and sometimes the nature of interparticle forces.

Plasticizers or superplasticizers provide steric hindrance that reduces the attractive forces at the origin of yield stress [1]. In contrast, flocculants adsorb on several particles simultaneously and increase yield stress [2,3] through polymer bridging. Chemical admixtures, which have no affinity with the cement particles or which remain in the suspending fluid as the cement surface is saturated, have extensively been studied for their stabilizing effect and/or enhancement of the material water retention capability [4–7]. However, there exist very few studies on the rheology of cementitious materials dealing with the possible impact on yield stress of these non-adsorbing polymers [8,9].

It is well known in the literature of colloidal particles that the addition of non-adsorbing polymer to a suspension can greatly affect the inter-particle interactions [10–29]. When a polymer has no affinity with

an interface, its conformational entropy loss cannot be compensated by adsorption energy and it is excluded from the interface leading to a formation of a region of pure solvent. The difference in polymer concentration between bulk solution and depleted zones leads to an increase in osmotic pressure [30]. This in turn generates so-called depletion attractive forces, which may cause particle flocculation. In cementitious materials, the consequences of depletion forces are still unclear and contradictory results have been reported. A major source of difficulty in the study of polymers in cementitious materials lies in their partial adsorption.

According to [8,31,32], viscosity-enhancing admixtures could be at the origin of both bridging and depletion flocculation. On the contrary, other authors [3] suggest from first order calculation that depletion forces in cementitious materials are not large enough to explain the magnitude of the measured yield stress variations. As the rheological behavior of cementitious materials is dictated by the nature and intensity of cement particles interactions, the understanding and prediction of the mechanism of action of non-adsorbing polymers become of utter most importance for the mix design engineer.

This study aims for a more fundamental understanding of the flocculation mechanism due to non-adsorbing polymers. We study how

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such polymers (i.e. Polyethylene glycol), with molar masses varying over several decades, affect the yield stress of cement and calcite pastes. Inert suspensions of calcite are used as a model system for cement. Polymer dosages cover a range of practice relevant values, both in the dilute and the semi-dilute polymer concentration regimes. We choose to use mainly rheology to understand the role of non-adsorbing polymers and identify their mechanisms of action in a cement paste.

From the models proposed in literature, we estimate interparticle forces and correlate them to the yield stress of the suspension. Our results suggest that non-adsorbing polymers are at the origin of depletion attractive forces in both cement and calcite pastes, the magnitude of which mainly depends on polymer concentration rather than molecular weight.

2. Materials and protocols

2.1. Materials

2.1.1. Powders

The cement used in this study is an ordinary Portland cement, a CEMI according to the European standards. Its chemical composition is obtained through Inductively Coupled Plasma and Atomic Emission Spectrometry (ICP-AES Horiba ultima 2000) and Thermogravimetric and Differential thermal analysis (ATD-ATG NETZSCH STA 409E). The Bogue composition is given in Table 1. The free lime content was determined by extraction with hot ethylene glycol [33]. The cement powder maximum packing fraction was estimated to be around 60% in [34], its Blaine specific surface is $3650 \pm 100 \text{ cm}^2/\text{g}$ and mean volume particle diameter measured by laser diffraction scattering (MALVERN MASTERSIZER S) dispersed in isopropanol is $10 \mu\text{m}$. The calcite (CaCO_3) used in this study was purchased from Sigma Aldrich. Its mean volume particle diameter measured by laser diffraction scattering (MALVERN MASTERSIZER S) dispersed in water is $1.4 \mu\text{m}$. The particle size distributions of cement and calcite are plotted in Fig. 1.

2.1.2. Polymers

Two superplasticizers having the same average molecular structure were used in this work to tune the magnitude of the Van der Waals attractive forces in the studied pastes. The superplasticizer used in cement pastes was prepared specifically for this study by the Dow Chemical Company® through an esterification process whereas the superplasticiser used in calcite suspensions was synthesized by esterification and provided by Sika. They are both comb-copolymers (PCE) in the flexible backbone worm regime as defined in [35]. They are both poly-carboxylates with methacrylic acid backbone and polyethylene oxide side chains terminated by methyl groups. Their molecular structure is shown in Fig. 2a. The number of monomers in the backbone is in average 60 whereas each side chain contains in average 23

Table 1

Chemical and Bogue composition of the Portland cement.

Chemical composition		Bogue mineralogical composition	
CaO	61,89%	C ₃ S	65.47%
SiO ₂	19,08%	C ₂ S	5.31%
Al ₂ O ₃	3,63%	C ₃ A	2.56%
MgO	0,72%	C ₄ AF	12.70%
MnO	0,05%	Gypsum	5.25%
SO ₃	2,44%	CaO free	0.78%
Fe ₂ O ₃	4,18%	Calcite	0.48%
Na ₂ O	0,27%		
K ₂ O	2,73%		
TiO ₂	0,22%		
Cl-	0,07%		
Insoluble residue	2,13%		
Loss on ignition	2,25%		
Sum	99,66%		

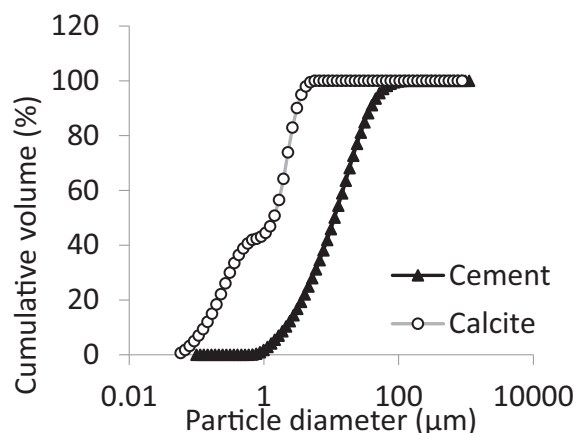


Fig. 1. Particle size distribution of cement and calcite.

monomers. The grafting ratio is 1/3 and the polymer molar mass, computed from its molecular structure, is approximately 20,000 g/mol. Grafting density was determined from stoichiometry of reactants. Polymers were ultrafiltered to remove possible residues (Labscale TFF System, Merck Millipore, with a membrane Pellicon XL Biomax 5KDa).

Three Polyethylene oxide glycol products (PEG) provided by Dow Chemical were also used in this work to generate depletion forces. Polyethylene glycol is a linear polymer, which is synthesized by ionic polymerization of ethylene oxide utilizing metal alkoxide compounds as catalysts [36,37]. Its molecular structure is shown in Fig. 2b. Molar masses and radius of gyration measured by Size Exclusion Chromatography (SEC) are gathered in Table 2. The critical overlapping concentration c^* which separates dilute and semi-dilute regime is computed as $c^* = M_w/N_A R_g^3$ (see Table 2). We recall that in the dilute regime, polymer coils in the solvent are far from one another (i.e. there is no contact between them) and display the same conformation as if they were alone. Above a critical overlapping concentration c^* , polymer coils decrease their apparent volume by interpenetrating their chains. This is the semi-dilute regime. The critical overlapping concentration c^* depends on the approximations made regarding the shape, the volume and deformability of the polymer coils.

SEC measurements were carried out with a Malvern Viscotek TDA 302 system equipped with a refractive index detector. Three columns in series OHPak SB-806 M HQ were used. An aqueous solution containing 0.2 M NaNO_3 was used as eluent. All samples analysis was conducted after an injection of 100 μl at a flow rate of 0.7 ml/min.

2.2. Sample preparation

Cement and calcite pastes were respectively prepared with mass ratios of Liquid/Solid of 0.4 and 0.55. Only the dosage and the PEG varied from one sample to another. The cement pastes were prepared by mixing 250 g of cement powder and 100 g of aqueous solution containing PEG and 1% of PCE. The pastes were first homogenized by hand and then mixed during 1 min using a Turbo test Rayneri VMI mixer at 840 rpm. After 15 min of rest, the samples were mixed again during 1 min. The calcite pastes were prepared by mixing 250 g of calcite powder and 137.5 g of aqueous solution containing PEG and 1% of PCE. The pastes were mixed at room temperature and stirred for 3 min at 800 rpm with a EUROSTAR power control equipped with a 4-bladed propeller paddle. The suspension was then placed in a sonicator for 1 min. To carry out rheological measurements, the paste was placed directly in the cup of the rheometer. For adsorption measurements, cement pore solutions were extracted by centrifugation while calcite pore solutions were extracted by using a stainless-steel pressure filter holder equipped with a $0.45 \mu\text{m}$ membrane filter.

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